ACTA MINERALOGICA-PETROGRAPHICA, FIELD GUIDE SERIES, VOL. 30, 1–23.

ACTA Mineralogica Petrographica

Clays, (palaeo-)environment and culture: Field trip in Southern Transdanubia, Hungary

BÉLA RAUCSIK[1*], GÁBOR ÚJVÁRI[2] AND ISTVÁN VICZIÁN[3]

[1] Béla Raucsik, Department of Geology, University of Pécs (PTE), Pécs, Ifjúság útja 6, H-7624 Hungary; raucsik@almos.uni-pannon.hu, *corresponding author

[2] Gábor Újvári, Geodetic and Geophysical Research Institute of the Hungarian Academy of Sciences (MTA GGKI), Sopron, Csatkai E. u. 6-8, H-9400 Hungary; ujvari@ggki.hu

[3] István Viczián, Geological Institute of Hungary (MÁFI), Budapest, Stefánia út 14, H-1143 Hungary; viczian@mafi.hu

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1. Introduction

(Attila Vörös & Béla Raucsik)

1.1. Terranes of the Alpine–Carpathian–Pannonian region

Palaeomagnetic, palaeobiogeographic, stratigraphic, facies and structural comparisons of different parts of the Alpine–Carpathian region suggest that four major Palaeogene terranes build up this area (Csontos & Vörös, 2004). These are named here the Alcapa, Tisza, Dacia and Adria terranes (Fig. 1). All of them are composed of different Mesozoic geodynamic units and were assembled during a complex Late Cretaceous – Paleogene history (Csontos & Vörös, 200 4).

On the basis of palaeomagnetic data, tectono-stratigraphic evolution and typical Early Jurassic fauna belonging to two major faunal provinces, it was concluded that the above terranes existed as more or less individual microcontinents in the Mesozoic Tethys (Vörös, 1993, 2001; Csontos & Vörös, 2004). The major parts of the Alcapa and Adria terranes are thought to be former parts of the Mediterranean microcontinent, inside the Tethys Ocean. The bulk of the Tisza and Dacia terranes were formed by parts of the large Tisza–Getic microconti-

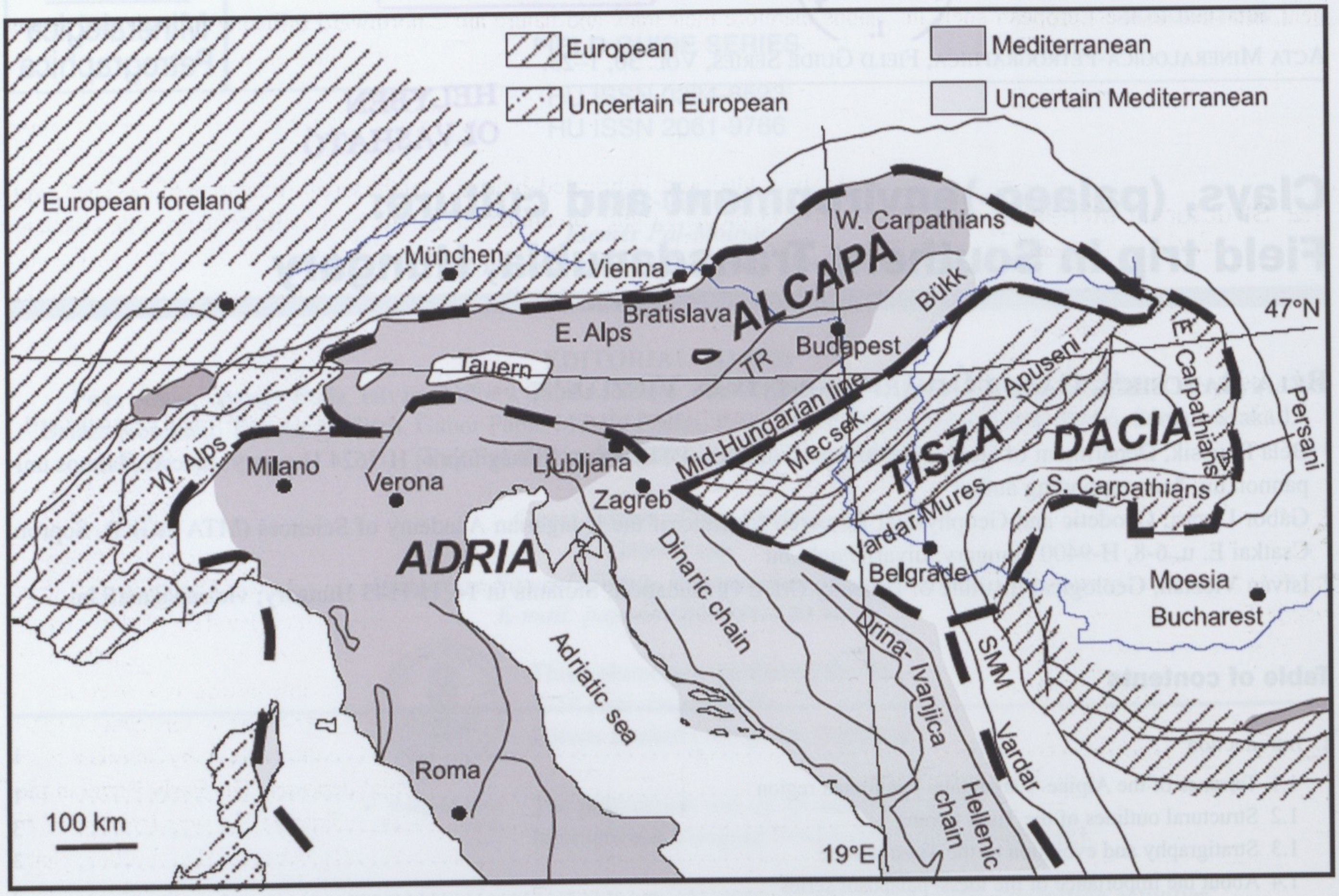


Fig. 1. Major terranes of the Alpine–Carpathian–Pannonian region shown on a palaeobiogeographic map for the first half of the Jurassic (Sinemurian–Bathonian). TR – Transdanubian Range, SMM – Serbo–Macedonian Massif (From Csontos & Vörös, 2004).

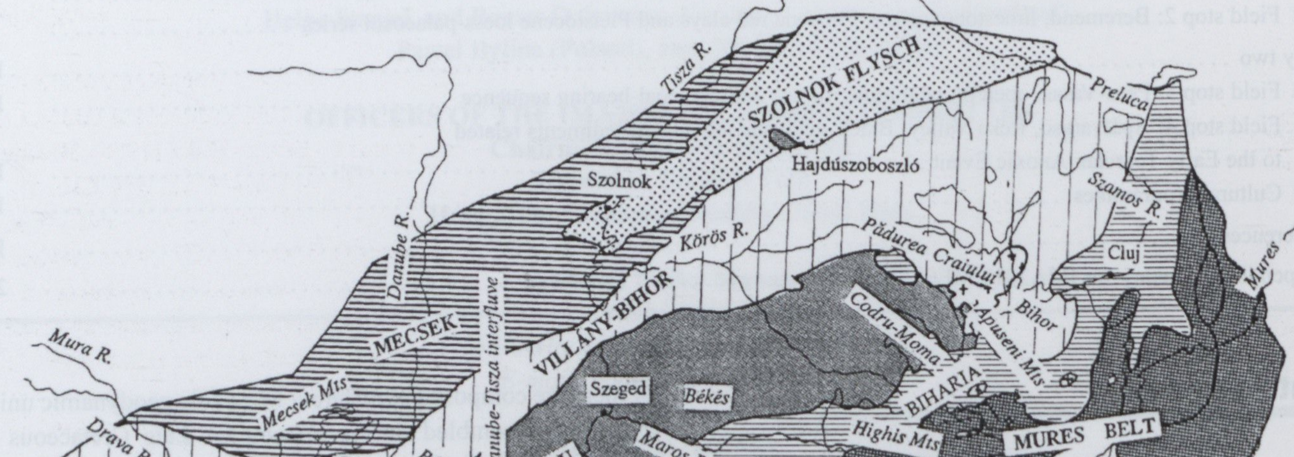


Fig. 2. Structural sketch map of the Tisza terrane (From Vörös & Csontos, 2006).

nent, attached to the European shelf in the first half of the Mesozoic, and separated and drifted into the Tethys from the Middle Jurassic.

1.2 Structural outlines of the Tisza terrane

This roughly triangular, more than 500 km long and less than 300 km wide terrane occupies the southeastern half of the intra-Carpathian area (Fig. 2). Its crystalline and Mesozoic rocks appear on the surface only near the eastern and western terminations; the intervening part forms the basement of the Great Hungarian Plain and is covered by very thick (locally attaining 6,000 m) young Tertiary sediments.

The tectonic lines delimiting the Tisza terrane run in young sedimentary depressions therefore their track and nature are not known exactly. The western and eastern terminations are very vague; the northern boundary is the Mid-Hungarian Lineament whereas in the south a continuous, strongly folded and imbricated belt of "Vardar elements" (with predominant Jurassic ophiolites) is thrust over the margin of the Tisza terrane proper.

The Tisza terrane can be subdivided into four tectono-sedimentary units which trend from the WSW to ENE, subparallel with the Mid-Hungarian Lineament. These are (from N to S): the Mecsek zone, the Villány–Bihar (Bihor) zone, the Lower Codru Nappes and the Upper Codru + Biharia Nappes. A separate unit, lying on the southern margin of the Tisza terrane, is the Maros (Mureş) belt.

The Mecsek and the Villány–Bihar zones have relatively simple structure; northward thrusting prevails and strong imbrications occur frequently. True nappes are not proved in the surface outcrops but there are strong hints to nappe-like large-scale thrust sheets in the basement of the Great Hungarian Plain. The Codru units have definite nappe-pile character though it is manifested only in the surface outcrops in the Transsylvanian Mid-Mountains (Apuseni Mts).

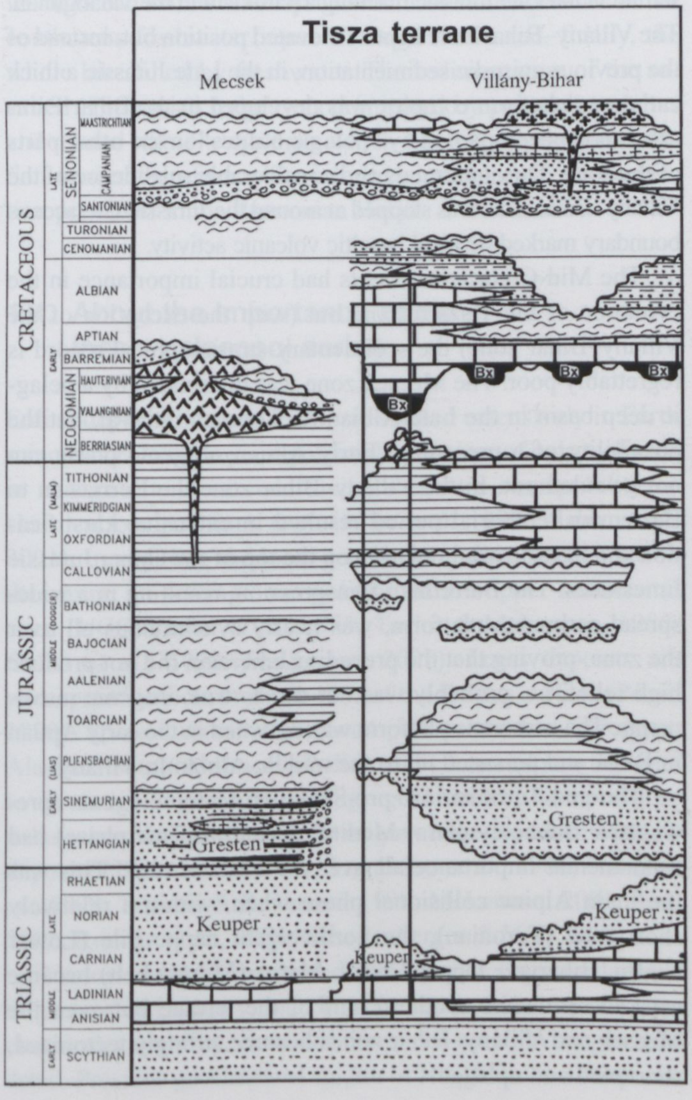


Fig. 3. Chronostratigraphic chart of the Mecsek and Villány–Bihar (Bihor) zones of the Tisza terrane. The framed part of the formations crops out in the Villány Hills.

1: shallow marine or lacustrine siliciclastic sediments and coal measures, 2: deeper marine marly sediments, 3: shallow marine, mostly platform carbonates, 4: pelagic and/or deep sea sediments free of terrigeneous clastics, 5: alkaline and/or tholeiitic volcanic rocks, 6: calc-alkaline volcanic rocks, 7: flysch-like turbititic sediments, Bx: bauxite (modified after Vörös & Csontos, 2006).

1.3 Stratigraphy and evolution of the Tisza terrane

In the southern part of Transdanubia, the crystalline basement is composed of Early Paleozoic – Lower Carboniferous granites, migmatite, clay slate, phyllite and serpentinite. South of the mountains these rocks are unconformably overlain by Upper Carboniferous terrigenous sandstones, in the Mecsek by Permian continental deposits. The Early Permian molasse sedimentation was interrupted by continental rifting related rhyolite volcanism, then the returning fluvial accumulation changed into lacustrine one. This latter is represented by the so-called Boda Siltstone Formation. After that, a fluvial sequence was deposited in the Late Permian; its uppermost unit extends into the Early Triassic.

The Mesozoic stratigraphy of the Tisza terrane is summarized on the basis of the works by Bérczi-Makk (1986), Bleahu *et al.* (1994), Császár (2002), Csontos & Vörös (2004), Haas (2001) and Vörös & Csontos (2006). The Mesozoic sedimentary history starts with a very extensive and rapid transgression in the earliest Triassic. The basement, i.e. the peneplained land surface invaded by the sea, was made up by Permian sandstones, conglomerates and volcanites or locally (in the southwest) by older metamorphic rocks. Correspondingly, the major part of the Scythian consists of conglomerates and thick sandstones. Diminution of grain-size and decrease of the amount of the terrigeneous clastics gradually leads to the deposition of pure carbonates in the Early Anisian. In the Mecsek–Villány region the shallow-water carbonate sedimentation continued up to the end of the Ladinian (Fig. 3).

A very important regional change can be recorded at the Ladinian/Carnian boundary when the sedimentation switched from carbonate to clastic in the Mecsek and Villány. The character of the sedimentation and the geometry of the sedimentary basins seem to have been governed by a newly formed, first order fault line between the Mecsek and Villány zones. Due to the strong strike-slip component of this master fault, a southward tilting half-graben has been developed in the Mecsek zone filled up with an enormously thick Upper Triassic "Keuper" type (sandstone/clay) sequence. At the same time, the neighbouring Villány zone suffered a differential uplift, erosion and on the rugged surface thin "Keuper" type sediments accumulated in local basins (Fig. 4). This terrigeneous influx (implying an ultimate source in the European continent) appears in a more diluted form in the southern (Lower Codru) units.

In the Mecsek zone, the previous terrigeneous sedimentation continues uninterruptedly in the earliest Jurassic. Important change is the mass accumulation of coal measures first in fresh water then brackish and marine environment. This testifies that

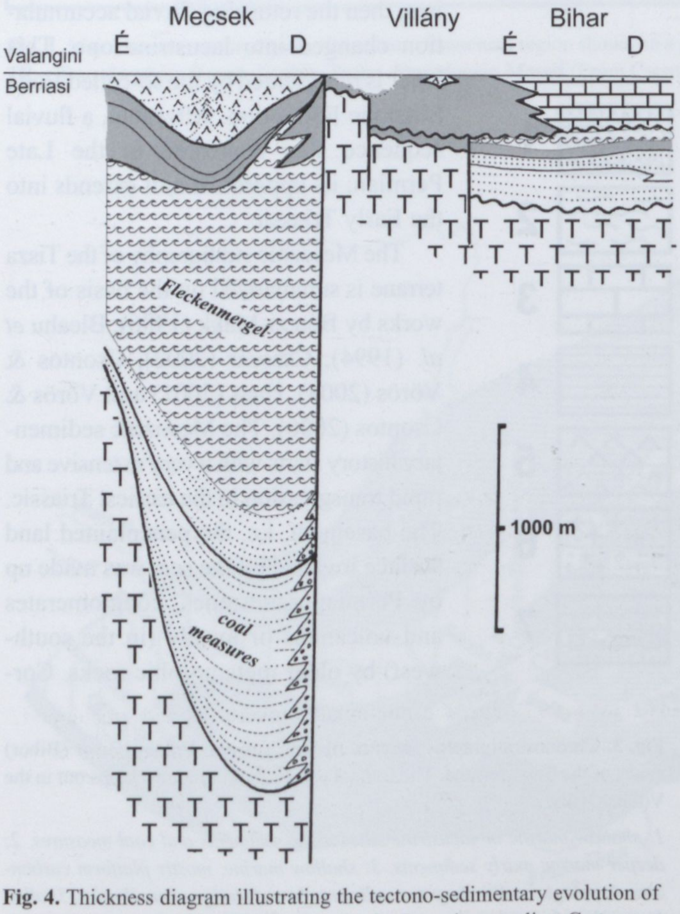


Fig. 4. Thickness diagram illustrating the tectono-sedimentary evolution of the northern zones of the Tisza terrane in the Jurassic to earliest Cretaceous (modified after Vörös, 2006).

the subsidence of the tectonic graben continued at a high rate. From the Sinemurian onwards, the marine basin reached a greater depth and the sediment became predominantly marly but the subsidence remained very rapid until the Bajocian. The important Early Toarcian anoxic event produced a thin but extremely organic-rich black shale formation all over the Mecsek basin.

The other zones of the Tisza terrane show a peculiar palaeogeographical pattern in the first half of the Jurassic. The Villány–Bihar zone and the Upper Codru Nappes behaved as relatively elevated (either subaerial or submarine) ridges while the sedimentary zone of the Lower Codru Nappes sunk to a basinal position. In the Villány–Bihar zone the uplift started in the Late Triassic and the land was invaded by the sea diachronously: from the Hettangian (Bihar) to the Early Pliensbachian or Aalenian (Villány region). Correspondingly, the marine basin reached a greater depth and the sedimentary sequence was thicker and more complete in the Bihar while in the Villány the episodic deposition has resulted in very reduced and local sedimentary bodies.

The second half of the Jurassic shows marked changes all over the Tisza terrane. In the Mecsek zone the rate of sedimentation suddenly decreased, pelagic and cherty limestones and radiolarites have been accumulated and submarine basaltic volcanism started in the Late Iurassic reaching a paroxism in the Valanginian. The Villány–Bihar zone kept its elevated position but, instead of the previous episodic sedimentation, in the Late Jurassic a thick carbonate platform complex was developed in the Bihar Parautochthon accompanied by "pelagic oolites" in the other parts of the zone. The continuous and considerable subsidence of the Villány–Bihar zone was stopped at around the Jurassic/Cretaceous boundary marked by local basaltic volcanic activity.

The Mid-Cretaceous events had crucial importance in the evolution of the Tisza terrane but (with the exception of the Villány–Bihar zone) the sedimentary-stratigraphical record is regrettably poor. The Mecsek zone was dominated by a pelagic deep basin in the Late Albian to Turonian interval, but the possibility of a preceding, Early Albian orogenic phase can not be ruled out. In the Villány–Bihar zone the Berriasian to Barremian terrestrial period resulted in extensive karstification and bauxite accumulation on the top of the Upper Jurassic limestones. The Barremian transgression, resulting in a widespread carbonate platform, was nearly synchronous all over the zone, proving that the preceding emersion did not produce high relief, i.e. probably was not due to true orogenic movements. The carbonate platform was drowned in the early Aptian in Bihar and persisted up to the middle Albian in Villány.

The end-Turonian or pre-Senonian tectonic events (pre-Gosau = Subhercynian = Mediterranean orogenic phase) had fundamental importance all over the Tisza terrane. This was the main Alpine collisional phase when, within a relatively short time (Turonian), the northvergent nappe pile (Lower Codru, Biharia + Upper Codru, Maros (Mureş) belt) became stacked up on the southern half of the terrane but even the Mecsek and Villány–Bihar zones became strongly tectonized, shortened and uplifted.

For the Coniacian the present-day structural framework of the Tisza terrane was more or less completed and the basal clastic sediments of the Senonian transgressive cycle overlap the nappe structures. The Senonian sedimentary cycle starts with coarse grained clastics followed by shallow marine sandstones and marly intercalated with rudist (hippuritid) "reef" limestones. Gradual deepening led to the formation of deep water pelagic marls in the northern zones. The Senonian cycle is enriched by the important "banatite magmatism". Rhyolite tuffs appeared in the Campanian. Huge subvolcanic bodies and large rhyolite lava flows commenced in the Maastrichtian. The Cretaceous/Paleogene boundary is marked by a widespread unconformity in the Tisza terrane. The renewed strong compression (Laramian phase) led to the consumption and folding of the Senonian basins and to regional uplift of all units of the Tisza terrane.

The relative thick Permo-Mesozoic sedimentary pile of the Tisza terrane is covered by Lower Miocene continental siliciclastics and volcanics after an erosional gap and hiatus. Significant marine deposition in the area lasted during the Badenian-Sarmatian. During the Late Miocene, conditions of the normal marine sedimentation are drastically changed: the sea located in the Pannonian Basin was separated from the world ocean and its water mass went less saline because of the continuous freshwater input via large rivers and, finally, the whole lake filled by freshwater. The sedimentation of the so-called 'Pannonian Lake' was dominated by prograding deltas and related turbidite systems, which filled up the accommodation space; therefore a fluvial-pluvial and lacustrine deposition prevailed in the Pannonian Basin.

1.4. About the importance of the loess–palaeosol series

Eolian deposits, such as loess, are studied extensively in Earth sciences because they are potential indicators of palaeoclimatic change via preserved fossils, magnetic susceptibility or chemical compositions (*e.g.* Gallet *et al.*, 1996; Jahn *et al.*, 2001). In addition, the loess geochemical data can be used to determine the average composition of the upper continental crust (UCC; Taylor *et al.*, 1983; Taylor & McLennan, 1985; Gallet *et al.*, 1998; McLennan, 2001). Loess deposits are widespread and cover about 10% of the Earth's surface (Pécsi, 1990). Special attention has been paid to western European, Alaskan, South American, Indian and Chinese loess deposits to investigate geologic setting, geochemical composition, palaeoclimatic records and the origin and provenance of these deposits (Taylor *et al.*, 1983; Lautridou *et al.*, 1984; Gallet *et al.*, 1998; Tripathi & Rajamani, 1999; McLennan, 2001; Sun, 2002; Roddaz *et al.*, 2006; Schellenberger & Veit, 2006).

Factors leading to the deposition of loess–palaeosol sequences in Hungary and contributing to their internal geochemical variability, however, have not been investigated in detail. Previous geochemical studies of Hungarian loess deposits analyzed only for major elements were not placed into palaeoenvironmental framework (Pécsi-Donáth, 1985). Based on major and trace element geochemistry of loess–palaeosol series in Transdanubia, Hum & Fényes (1995) and Hum (1998, 2002) suggested that reconstruction of palaeoclimatic trends is possible. However, these authors described geochemical data without any modern provenance and palaeo-weathering interpretations. Previous source area interpretations identified 3 main sources of loess deposits in Hungary: (I) glacial materials carried through the Moravian Depression by glacial floodwater, (II) weathering products of the Carpathian Flysch, and (III) glacial materials from the Alpine region (Smalley & Leach, 1978; Pécsi, 1993). An alternative explanation was offered by Smith *et al.* (1991), who inferred a dominantly local source for Hungarian loess, suggesting that the Pannonian deposits (marine and shallow lacustrine deposits of conglomerates, sandstones, clays, marls, and sands) occurring subsurface in the Great Hungarian Plain formed in the Pannonian s.l. epoch (equivalent to Pliocene and upper part of Miocene, ~1.8–12.6 Ma; Rónai, 1985) could theoretically contribute materials to the loess deposits. On the other hand, Wright (2001) emphasized the cumulative effects of several silt-sized quartz-producing mechanisms (aeolian abrasion, fluvial comminution, glacial grinding, frost weathering) and sorting processes during the formation of loess deposits in Hungary on the basis of previous laboratory simulations (Wright *et al.*, 1998). She suggested that the source rocks of these loess deposits might be originating north of the Moravian Depression and local, possibly Pannonian sediments.

Geochemical studies of fine-grained sediments have contributed significantly to the determination of the average upper continental crust composition (Taylor & McLennan, 1985; Schnetger, 1992; Gallet *et al.*, 1996, 1998; McLennan, 2001). Schnetger (1992) presented an average loess composition (AVL1) including the values for seven loess regions from a variety of depositional scales, and McLennan (2001) redetermined an average Quaternary loess composition (AVL2) from the mean of eight regional loess averages from New Zealand, central North America, Kaiserstuhl region (Germany), Spitsbergen (Norway), Argentina, United Kingdom, France, and China. Detailed geochemical investigations of loess deposits worldwide contribute to the accurate determination of average loess composition, which is particularly fruitful in establishing the average composition of the upper continental crust (Taylor *et al.*, 1983; Taylor & McLennan, 1985; Schnetger, 1992; Gallet *et al.*, 1996, 1998; McLennan, 2001).

1.5 Review of the red clay and loess–palaeosol stratigraphy in Hungary

Wide lands of Hungary are covered by Quaternary unconsolidated sediments including Pleistocene loess deposits with variable thickness (10–70 m). Underlying the loess–palaeosol

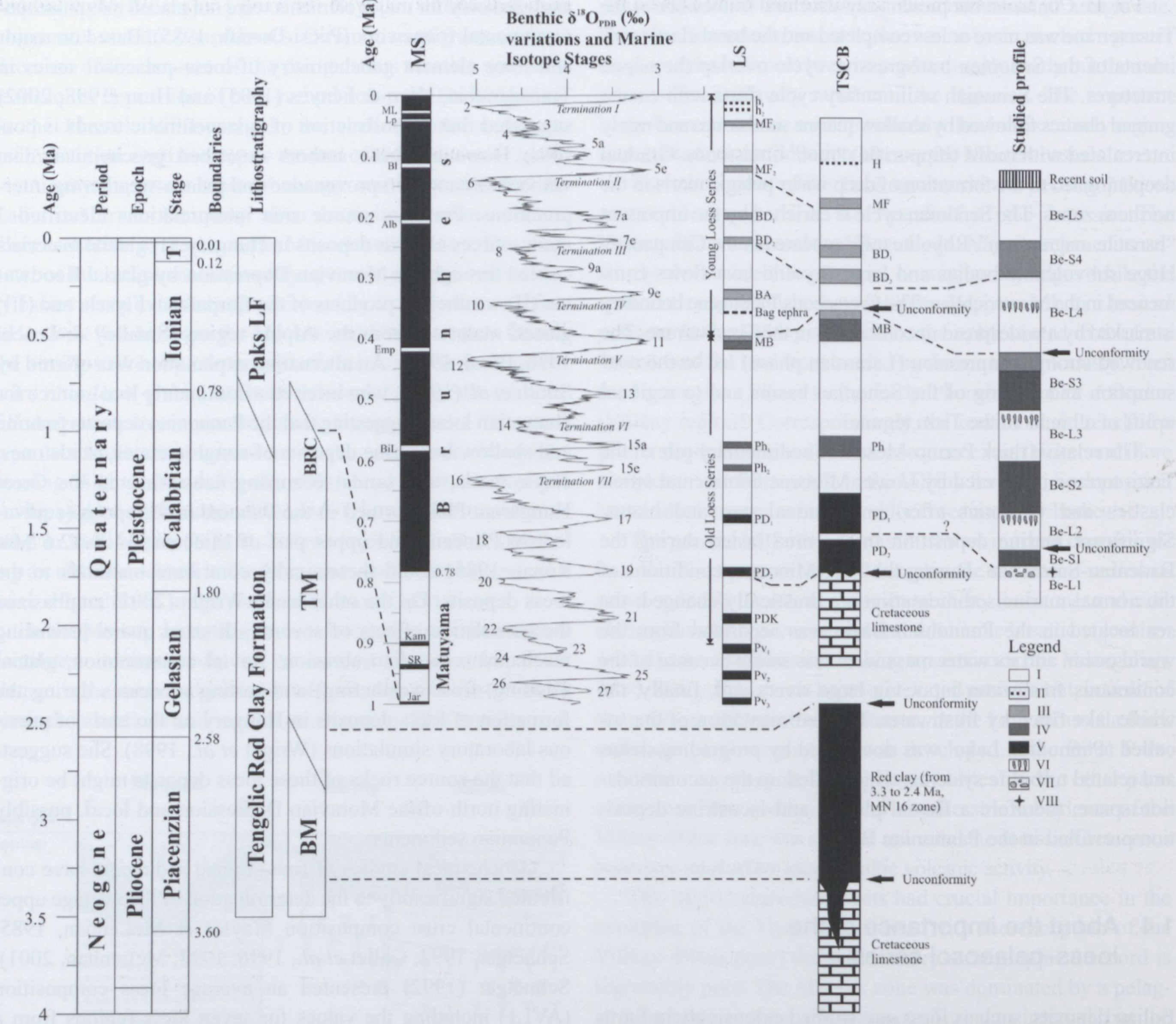


Fig. 5. Geochronological and stratigraphical framework of the Hungarian red clays and loess–palaeosol sequences with the stratigraphic position of the studied profile at Beremend. Global chronostratigraphy is from Gibbard & Cohen (2008). T = Tarantian, Paks LF = Paks Loess Formation, BM = Beremend Member, TM = Tengelic Member, BRC = Basal Red Clays of the Paks Loess Formation (after Pécsi, 1985a,b; Kretzoi, 1987; Schweitzer & Szöőr, 1997; Koloszár, 2004; Marsi & Koloszár, 2004; Kovács, 2008). Palaeomagnetic record (MS = magnetostratigraphy) is from Singer *et al.* (2002), black corresponds to normal polarity. Abbreviations of the events: ML = Mono Lake, Lp = Laschamp, Bl = Blake, Alb = Albuquerque, Emp = Emperor, BiL = Big Lost, Kam = Kamikatsura, SR = Santa Rosa. Benthic $\delta^{18}O$ curve is the LR04 Stack of Lisiecki & Raymo (2005). LS = loess–palaeosol stratigraphy in Hungary (framework and abbreviations are from Pécsi, 1995) with some modifications after Koloszár & Marsi (2005): H1 = "Tápiósüly" humus horizon, H2 = "Dunaújváros" humus horizon, MF1 = Mende Upper 1 palaeosol, MF2 = Mende Upper 2 palaeosol; BD1 = Basaharc Double 1 fossil soil, BD2 = Basaharc Double 2 fossil soil, BA = Basaharc Lower palaeosol, MB = Mende Base palaeosol, PH1-PH2 = Paks sandy soil complex, PD1 = Paks Double 1 palaeosol, PD2 = Paks Double 2 palaeosol, PDK = Paks-Dunakömlőd soil complex, PV1-PV3 = basal red soils/red clays. Correlation of loess and palaeosol layers with the $\delta^{18}O$ record is after Gábris (2007), but slightly modified. TSCB = theoretical stratigraphic column on the Szőlő Hill at Beremend (after Marsi & Koloszár, 2004). Be-L1 to L5 = loess layers in the studied profile, Be-S1 to S4 = palaeosol horizons. Legend (for theoretical columns and the studied profile): I = loess, II = humus horizon (syrosem), III = forest steppe type palaeosols (chernozem-brown forest soil), IV = brown forest soils, V = Mediterranean type palaeosols (terra rossa)/red clays, VI = carbonate concretions, VII = crotovinas, VIII = appearance of the species *Neostyriaca corynodes*.

sequences red clays can be found frequently settled on Upper Pannonian deposits of Late Miocene to Early Pliocene age (Magyar, *et al.*, 1999; Koloszár, 2004). Middle Pliocene to Lower Pleistocene (~3.3 to 0.8 Ma) terrestrial red clays in Hungary are assigned to the Tengelic Red Clay Formation (Koloszár, 2004; Kovács, 2008; Fig. 5).

Terra rossa-like red clays of the Beremend Member of the Tengelic Formation filling fissures and recently existing caves in limestone of the Villány Hills were formed between 3.3 and ~0.8 Ma (Jánossy, 1992, 1996; Marsi & Koloszár, 2004). The Tengelic Member's red clays cropping out only sparsely in some places were firstly described by Pécsi *et al.* (1979a, 1979b, 1979c) from boreholes at Dunaföldvár and Dunakömlőd. Based on palaeomagnetic data Pécsi *et al.* (1979c) concluded that the formation of these more than 30 m thick clay, silt, and red clay sequences called the Dunaföldvár Complex took place between 4 and 0.9 Ma. The Tengelic Member consisting of red–reddish-brown and variegated clays, silts and sands was named after yet another drill core (Tengelic T-2) and the name coined by Pécsi *et al.* (1979c) was discarded (Koloszár, 2004). According to palaeomagnetic data and calculated sedimentation rates of the Tengelic T–2 and Udvari U–2A cores the sediments of the Tengelic Member were deposited from 2.2 to 0.9 Ma during the Matuyama chron (Fig. 5; Koloszár, 2004). There was a continuous sedimentation around 1.0–0.9 Ma on hills in Middle Hungary (*e.g.*, Udvari, Paks), when the basal red clays formed (Fig. 5), therefore marking the boundary between the Tengelic Red Clay Formation and the Paks Loess Formation remained a controversial issue (Koloszár, 1997).

Two lithologic units have been distinguished within the Paks Loess Formation (Fig. 5): (1) Young Loess Series (YLS) (~13–380 ka; MIS 2–10) and (2) Old Loess Series (OLS; ~380–900 ka; MIS 11–22) (Pécsi, 1995; Gábris, 2007; see Fig. 5). The footwall of the Paks Loess Formation can be correlated with MIS-32 in the Udvari U-2A borehole (~1.1 Ma; Koloszár, 2010). The YLS can be subdivided to Dunaújváros–Tápiósüly (upper part) and Mende–Basaharc (lower part) sequences (Pécsi, 1993). OLS includes the lower and upper parts of the Paks sequence (Pécsi, 1993, 1995).

Three loess layers and three Mediterranean (terra rossa) type palaeosols (PDK, PD2, PD1; Fig. 5) constitute the lower part of the OLS while the upper part of OLS makes of three loess and brown forest soils (PH2, PH1, MB). Pécsi (1979) described an additional hydromorphous soil (Mtp) in the Paks sequence below the PH2 soil, but this palaeosol cannot be traced either in South-Hungarian boreholes (Koloszár & Marsi, 2005) or in natural outcrops at Beremend (Marsi & Koloszár, 2004). Correlation of the old fossil soils presented in Fig. 1 is only tentative and follow a recent work of Gábris (2007) with some modifications such as the omission of Mtp soil. The only one reference point in the OLS is the position of Matuyama–Brunhes Boundary (MBB) which was found by Pécsi & Pevzner (1974) and Márton (1979) below the PD2 palaeosol. These results were subsequently corroborated by Sartori *et al.* (1999) at Paks placing the MBB in the uppermost part of or above the PD_2 soil. This means that the given fossil soil formed during MIS 19, and the older PV_{1-3} and PDK soils deposited during the Matuyama chron. Correlation of the palaeosols PD_1 and PH_{1-2} with the $\delta^{18}O$ curve is exclusively based on the position of the MBB, so it seems to be a bit vague at this time.

The Bag tephra which is a widespread volcanological marker horizon in the YLS (lower part, Mende-Basaharc series) between the MB and BA soils is another chronological tie point in spite of its age being poorly constrained (~350-380 to 788 ka, Pouclet *et al.*, 1999; MIS 8 or 10, Horváth, 2001; Fig. 5). Proposed correlation with the Villa Senni Tuff, dated around ~351 ka (Pouclet, *et al.*, 1999), has been questioned in a recent study of Sági *et al.* (2008). At the same time, it has been suggested (Zöller, *et al.*, 1994; Oches & McCoy, 1995) that the assignation of MB soil to MIS 11 and BA to MIS 9 is very likely, this conception is supported by data from the Udvari U-2A borehole and from the Mórágy area (István Marsi, pers. commun.). It is worthy of note here that first TL studies (Zöller & Wagner, 1990, Zöller, *et al.*, 1994) referred to the fact that MB, BA and BD_{1-2} soils should be older than the last interglacial and Pécsi's loess chronostratigraphy (*e.g.* Pécsi, 1985a) is untenable (see Frechen, *et al.*, 1997). Correlation of BD_{1-2} forest steppe soils with MIS 7a-e stem from the conclusions of these TL dating works and from AAR data of Oches & McCoy (1995). The chronostratigraphic position and correlation of MF_2 and MF_1 palaeosols with MIS 5 and MIS 3 is nowadays well established owing to the mentioned TL and subsequent IRSL and AAR studies (Frechen, *et al.*, 1997; Novothny *et al.*, 2002; Oches & McCoy, 2001). Ages of the humic horizons (H_{1-2}) in the upper part of YLS are 16,750 ± 400 BP (17–19 ka cal BP) and 21,740 ± 320 BP year (23-25 ka cal BP) (Pécsi & Pevzner, 1974) corroborated by further ^{14}C (Sümegi & Krolopp, 2002), and TL-IRSL data (Wintle & Packmann, 1988; Novothny *et al.*, 2002).

2. Field stops

Day one

2.1 Field stop 1: Kővágószőlős; visit to the Mecsekérc Ltd. and Geochem Ltd. (sources: www.mecsekerc.hu, www. geochem-ltd.eu)

The Mecsekérc Ltd's legal predecessor performed its main activity, the uranium ore mining from 1955 to 1997. The mining and ore processing activities were followed by mine closure and remediation works, within the scope of production termination of professional way. Since 1993, the company has been taking part initially in the projects for the disposal of high-level, later for the low- and intermediate-level radioactive wastes. The company's activity has changed considerably in the preceding years. The large enterprise in charge of the uranium ore mining which having employed nearly 8,000 persons, has gradually changed to a flexible organization that can adapt to the actual requirements of life. The employees have university degree and adequate skill in the fields of mining, geotechnics, geology, hydrogeology, geophysics, geodesy, chemistry, energetics, environmental protection, remediation, mapping, soil mechanics and project management. The company has an accredited Analytical Laboratory for the special fields of sampling, radiometry, chemistry, environmental geology and soil mechanics. It has been built extended professional relations with the majority of the Hungarian professional enterprises, universities and academic research institutes. The Mecsekérc Ltd. undertakes the solution and accomplishment of environmental protection, geoscience, technical and geotechnical jobs on the following fields:

1. Design and implementing of repositories to be developed with mining techniques (*e.g.* prospecting for low- and intermediate-level radioactive waste repository, gas or LPG storages, pumping energy accumulator power plants).
2. Prospecting and preparation of interim or final disposal of radioactive and hazardous wastes, and the construction of facilities for these purposes.
3. Planning and fulfillment of the remediation activity for uranium industry in Central European countries.
4. Full-scale remediation and land reclamation activity to wind up the consequences of former mining and other environment-harming activities.
5. Soil mechanical test, control and design of earthworks.
6. Environmental damage assessment.
7. Planning, implementing and licensing of environmental damage remediation activities.
8. Geological, hydrogeological and mineral resource prospecting.
9. Geological, hydrogeological and soil mechanical planning and carriage tasks related with infrastructural investments (*e.g.* road and railway construction).
10. Testing, planning and carriage works for the protection and securing drinking water resources.
11. Surface and underground solid mineral mining activity, obtaining mining licenses.

Geochem Geological and Environmental Research, Consultancy and Service Ltd. is an economic company, working primarily in the field of geology. The Geochem Ltd. was established as a successor of Geochem Limited Partnership on March 2, 2006, in which Mecsekérc Ltd. has bought an ownership stake of 25% (January 23., 2008). In the coming years, Geochem Ltd. intends to concentrate principally on research and development activities. Its main objective is to integrate the results of basic research into industrial practice, in order to help in selling accumulated knowledge. To achieve this aim, they plan to employ highly qualified engineers, as well as scientific experts performing basic and applied research. The company has signed a co-operative agreement with several partners, planning common development work in the fields of geochemistry, geophysics and laboratory techniques.

The potential candidate to final disposal of the high-level nuclear power plant radioactive wastes is the so-called Boda Siltstone Formation (BSF). Geological mapping allowed the distinguishing of three main units within the formation (Fig. 6):

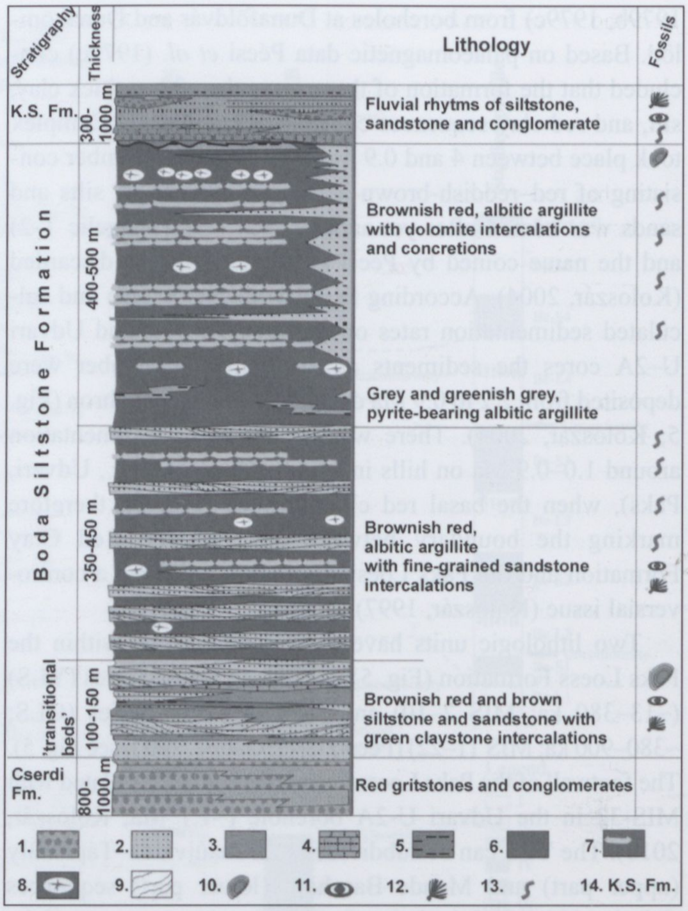


Fig. 6. Lithology of the Boda Claystone Formation.

Legend: 1 – conglomerate; 2 – sandstone; 3 – clayey sandstone; 4 – limestone; 5 – claystone; 6 – albitic claystone; 7 – dolomite; 8 – concretion; 9 – cross-bedding; 10 – phyllopod; 11 – sporomorph; 12 – macroflora; 13 – trace fossil; 14 – Kővágószőlős Sandstone Fm. (modified after Konrád, 2008).

1. Lower, 'transitional' sandstone (100 to 150 m), characterised by fine-grained sandstone beds.
2. Middle albitic claystone–siltstone with sandstone beds (350 to 450 m). It is characterised by cm or dm thick micaceous siltstone and fine-grained sandstone beds.
3. Upper claystone, albitic clayey siltstone and silty claystone with dolomite and siltstone beds, with desiccation cracks and in the upper part of the sequence with septarian dolomite concretions (400 to 500 m).

The BSF was deposited in a shallow-water lacustrine environment (playa mudflat, playa lake) under semi-arid to arid climatic conditions. The sediments of the BSF are red and reddish brown in colour, reflecting the dominantly oxidizing nature of the depositional and early diagenetic environment (Máthé, 1998; Árkai *et al.*, 2000).

Phyllosilicates (40-50%) such as illite ± muscovite and chlorite are the dominant minerals of the BSF. Mixed-layer chlorite/smectite, kaolinite and vermiculite were also identified in inconsiderable amounts. The different rock types of the BSF contain irregular or circular patches and lenses filled by mosaics of anhedral to subhedral plagioclase crystals (authigenic albite) with carbonate and barite and in few cases, authigenic K-feldspar and opaque minerals (galena, spharelite, chalcopyrite); these may represent some sort of void filling or mineral replacement. Some plagioclase has polysynthetic twinning and much is untwinned. Albite cementation was also recognized (Máthé, 1998). Based on observations of X-ray diffractometric and electron microprobe analyses, Árkai *et al.* (2000) proved that albite has the nearly pure Na-end member composition typical of ideal low-temperature albite indicating its authigenic origin. The authigenic albite content of this rock type is up to 40%, it varies generally between 20 and 35%. Quartz (5–15%), hematite (7–10%), and carbonates (up to 10%) are present in minor amounts. Carbonate occurs as dolomite and Mg(+ Fe,Mn)-bearing calcite rhombs and as microsparitic calcite cement representing a later generation phase. Siderite occurs only in few samples. Detrital grains of Ca-bearing plagioclase, K-feldspar, muscovite, biotite, chlorite, zircon, rutile, apatite, magnetite and ilmenite were also identified in inconsiderable amounts. In the lower part of the sequence, some rocks contain anhydrite-dominated veins with albite (Máthé, 1998).

2.2 Field stop 2: Beremend, Pliocene red clays and Pleistocene loess–palaeosol series

Red clays from the Beremend limestone quarry

The surface of the basement-forming Mesozoic limestones in the Villány area was covered by Middle Cretaceous, partly flysch-like clastic formations and later by Upper Pannonian (Miocene to Pliocene) sandy siltstone. During the Pliocene the Mesozoic block of the Villány Hills emerged, the covering sediments were eroded and karstification started. The covering Pannonian sediments are preserved only as light yellow unsorted sediments filling some open tectonic faults. Soils developed on the karstic surface were washed into the fissures and caves in various times, therefore indicating various degrees of weathering. Vertebrate fossils simultaneously washed in permit accurate age determination. 3 types of red clays can be distinguished (Dezső *et al.*, 2007; Viczián, 2007):

1. Terrestrial accumulation of red clays started in the Middle Pliocene, about 3.5 million years ago. In the first period intensely weathered red clays were formed. This type was preserved solely in karstic fissures and caves.
2. In the Upper Pliocene and possibly Lower Pleistocene a further, longer period is characterised by a weakly weathered type. In the Villány Hills, this type of red clays was preserved only in a few karstic fissures. In the broader surrounding, however, the weakly weathered type is widely distributed in waste areas of SE Transdanubia, and unconformably covers lacustrine Upper Pannonian sediments. In the stratigraphic nomenclature types 1 and 2 represent two members of the Tengelic Formation.
3. The Tengelic Red Clay Formation is unconformably followed by a further red clay, which is a red palaeosol on the base of the Middle to Upper Pleistocene loess complex (Paks Formation). The red palaeosol was preserved under the loess cover.

Red clays in the Villány Hills can be directly related to terra rossa of the Dinarides and of the North Hungarian Karst (Aggtelek, Esztramos).

As far as the granulometry of these sediments is concerned, distribution curves with a single maximum in the silt size domain are typical for the debris of the overlying Pannonian siltstone. Red clay fissure fillings display bimodal distribution curves with maxima both in the clay and silt domain. Some cave sediments have grain size distribution curves with a single maximum in the clay size domain.

The mineralogical composition was determined by X-ray diffraction in the bulk samples and in the < 2 μm fraction.

1. In the intensely weathered type of the Tengelic Formation the main clay mineral is strongly disordered kaolinite accompanied by smectite and mixed-layer kaolinite/smectite. There are anatase and rutile and gibbsite appears in lesser or medium amounts. Usually quartz is very low or missing. Normally hematite is more abundant than goethite among the iron minerals. In respect of highly disordered kaolinites and free Al-oxides this type is similar to the Pontian (Pliocene) Poltár Formation in Southern Slovakia.
2. In the weakly weathered type of the Tengelic Formation the clay minerals are represented by illite, chlorite, medium ordered kaolinite, variable smectite contents. There is fairly much quartz and feldspar. The iron mineral is dominantly goethite.
3. Basal red palaeosol the Paks Loess Formation contains similar minerals as the underlying weakly weathered type red clay. There are, however, slightly but significantly lower smectite and higher illite and chlorite contents in the < 2 μm fraction of red palaeosol.

Considering the climatic conditions, palaeontological and mineralogical results are in accord with each other:

1) The intensely weathered type corresponds to warm and humid subtropical or monsoon climate (similar to the present-day SE Asia).
2) The weakly weathered type represents semiarid savannah- and later steppe-type climate.
3) The composition of red palaeosol reflects further cooling before the onset of loess sedimentation.

The low hill at Beremend is separated from the main body of the Villány Hills by a Tertiary to Quaternary depression. At present, types of red clays can best be observed on this location due to extensive mining of Lower Cretaceous limestone (Fig. 7).

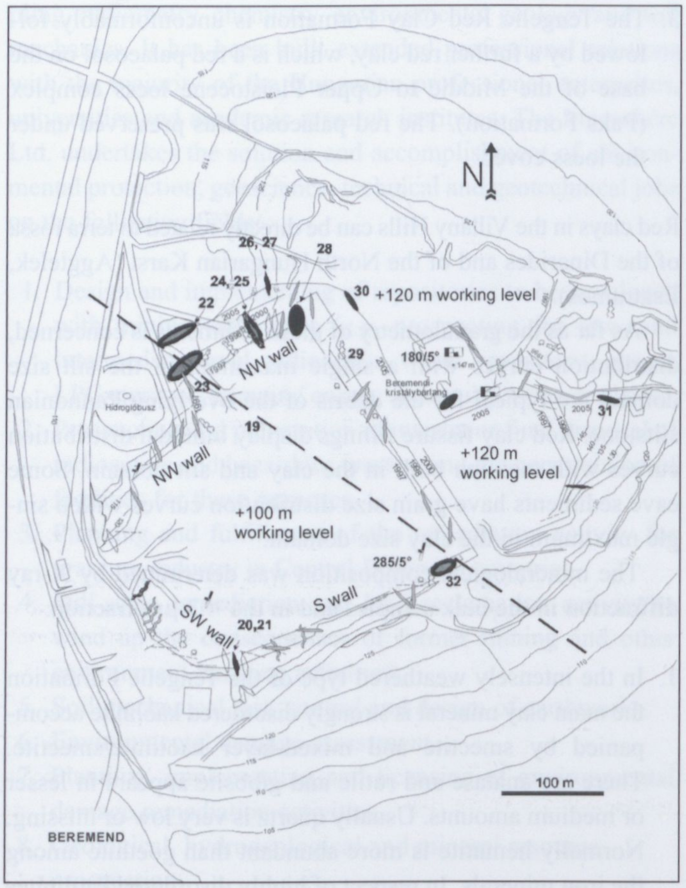


Fig. 7. Beremend, quarry of DDC Cement works. Black spots show intensely weathered red clay deposits. Grey spots show weakly weathered red clay deposits and palaeosol. Sample numbers are given. Light grey spots are calcite fissure fillings. On the +120 m working level a cave is under protection (= "kristálybarlang"). Map compiled by J. Dezső (see Dezső *et al.*, 2007).

Fissures were filled with karst water after the deposition of red clays which is indicated by the frequent calcite precipitation or cementation. Also empty voids in the red clay are ubiquitous.

1) Samples representing the intensely weathered type:

1a) Samples representing the most intensely weathered type (red bauxitic clay, No. 20 and 21). On the SW side of the quarry a single thin fissure was detected on the +100 m working level. The width of the fissure is only a few cm. The composition of its fill is rather special because it can be regarded as bauxitic red clay owing to its high gibbsite content. Bauxitic red clay was already described from the Beremend quarry by Császár & Farkas (1984). Its composition is not to be confused with the composition of the Lower Cretaceous Harsányhegy Bauxite Formation of the Villány Hill, which contains boehmite and diaspore but no gibbsite.

1b) Samples representing the typical intensely weathered type (No. 26, 30 and 31). These occurrences are found in the NE side of the quarry, farther away from the NW–SE trending fault line in the centre of the quarry. Their mineralogical composition is rather uniform. Typical is a few per cent of gibbsite (Fig. 8).

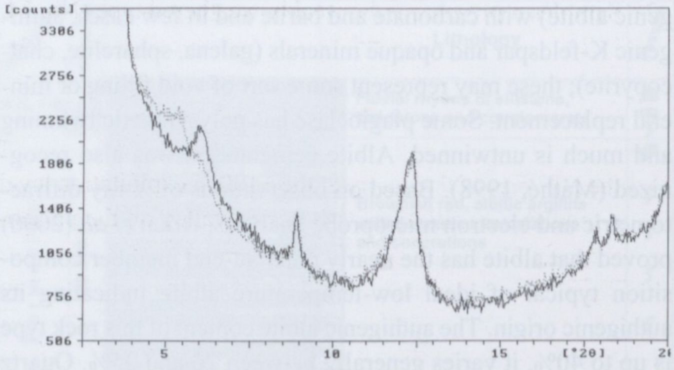


Fig. 8. X-ray diffraction pattern of the < 2 μm fraction of red clay fissure filling (sample No. 26), Beremend quarry. Intensely weathered type. Cu K_{α} radiation, oriented specimen. Continuous line: untreated sample, dotted line: ethylene glycol treated sample. Analysis made by B. Raucsik (see Dezső *et al.*, 2007).

1c) Sample representing transition between the intensely and weakly weathered type (No. 28). In the northern edge of the quarry there is a huge pile of red clays left behind by the mining works which represent the fill of a wide and deep karstic depression. The locality contains rich fossil Vertebrate fauna. Our sample No. 28 comes from the lower part of the pile, from a height of 105 m. The site has been thoroughly examined by Marsi & Koloszár (2004). X-ray diffraction analyses were carried out by Kovács-Pálffy on a large number of samples taken from the whole vertical section. According to these results the composition is quite homogeneous, there are no detectable differences in the mineralogical composition of its horizons. It agrees well with the assumption based on palaeontological studies of Kordos (2001) that the time of filling up of the depression took relatively short time in geological terms, approximately 200 thousand years (between 3.3-3.1 million years B.P.). During this time interval the features of the weathered material washed into the depression did not change visibly. The transitional nature of this occurrence is indicated by the presence of illite, chlorite and feldspars, and by quite much quartz. Typical is the lack of gibbsite.

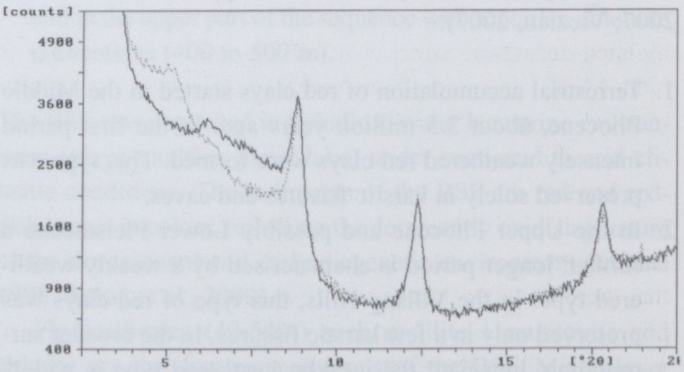


Fig. 9. X-ray diffraction pattern of the < 2 μm fraction of reddish palaeosol (sample No. 22) overlying the limestone, Beremend quarry. Similar to the weakly weathered type. Cu K_{α} radiation, oriented specimen. Continuous line: untreated sample, dotted line: ethylene glycol treated sample. Analysis made by B. Raucsik (see Dezső *et al.*, 2007).

2) Samples representing the weakly weathered type (No. 24, 25 and 32). The two localities of this type are close to the NW–SE fault line crossing the quarry. The red clays contain several tiny, fragile, angular bone rests.
3) Samples representing the palaeosol (No. 22 and 23). In the NW part of the quarry at the +100 m exploitation level a reddish clay fill of a fossil buried valley on the palaeosurface of the limestone can be observed, which forms the base of the loess series. The clay was studied before by Marsi & Koloszár (2004), who considered it to be a palaeosol belonging to the "Paks Double soil complex" in the loess stratigraphy (Fig. 9).

The quantitative relations of the clay minerals in these samples and their comparison with other localities of the Villány Hills are shown in Fig. 10.

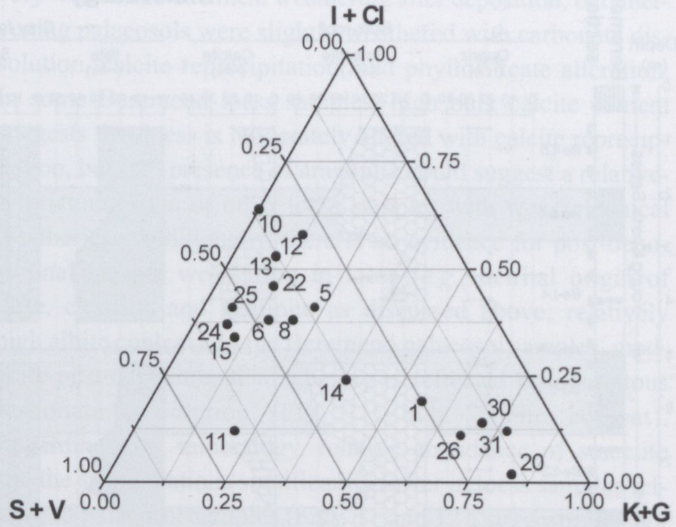


Fig. 10. Quantitative relations of clay minerals in the < 2 μm fraction of red clays in Beremend quarry and other localities in Villány Hills (see Dezső *et al.*, 2007). Legend: K + G: kaolinite + gibbsite % (products of intense weathering), S + V: (smectite + kaolinite/smectite) + (smectite + illite/smectite) + vermiculite % (products of moderate weathering), I + Ch: illite + illite/smectite + chlorite % (detrital minerals). At the points the sample number is given: *Samples 20, 26, 30, 31*: intensely weathered type of red clay. *Samples 24, 25*: weakly weathered type of red clay. *Sample 22*: red palaeosol. *Other samples*: other localities in Villány Hills.

The Beremend loess–palaeosol section

The Beremend loess–palaeosol section is located on the foothills of Hungarian mountains and on hills along the River Danube. The red clays are of Pliocene and Early Pleistocene age (Kovács, 2007, 2008), while the loess–palaeosol series from Beremend represents the upper part of the OLS and partially the YLS (Fig. 5) exposing the reddish brown forest soils of $PH_{1\text{-}2}$, MB and probably the MF_2 fossil soil. Correlation of the lower part of the section is based on an age-constraining, biostratigraphical data, the appearance of species *Neostyriaca corynodes* which lived between about 600 and 120 ka in the Carpathian Basin, and it could not be found in older (i.e. Lower Pleistocene) or younger (i.e. Upper Pleistocene) deposits up to now. This species appeared in a highly weathered loess layer at the bottom of Beremend section (10.80 m, Fig. 5) with a mild climate indicator fauna and in which did not appeared any cryophilous species. The *Neostyriaca corynodes* occurs in "loess fauna" which indicates cold climate only in loess deposits formed during the Riss glaciation, as long as its accompanying fauna indicates milder climate in older loess horizons formed during the Günz–Mindel glaciation. Based on this fossil record the bottom loess layer of Beremend section presumably accumulated during the Günz or Mindel glaciation. Assuming an older Middle Pleistocene age (Günz) for the basal loess layer and that the third (counted from the base), strongly developed and thickest pedocomplex is the MB soil because of its remarkable structural and genetical similarity to the stratotype soil (Pécsi, *et al.*, 1979; Újvári, 2005, 2006), the lower three palaeosols can be correlated with $PH_{1\text{-}2}$ and MB. It is worth mentioning that there is a significant unconformity on the top of the lowermost palaeosol (PH_2) showing itself as truncation of the soil (Fig. 5). Another unconformity can be found on the top of the third fossil soil (MB) which supports the findings of Marsi & Koloszár (2004) that the area was uplifted and eroded between about 280 to 170 ka. Presumably this period might be started before 280 ka because neither the Bag Tephra nor the BA soil could be uncovered above the MB soil. The uppermost fossil soil which is a less developed, brown forest or forest steppe soil can be hypothetically correlated with the MF_2 soil.

The bulk mineral composition of sediments estimated from XRD data indicates that quartz (~20–30%) and smectite (~10–40% in loess and ~40–60% in palaeosol) are the dominant minerals (Fig. 11). Interestingly, throughout both the loess and palaeosol units, relative proportion of quartz shows no variation. Loess samples contain high amounts of calcite (~10–40%); additionally, dolomite (< 10%) occurs in all loess samples and in the Be-S4 samples. Illitic material (illite ± muscovite) together with chlorite is present in all samples but usually in small proportion (< 5%), except for the Be-L1 samples in which illite ± muscovite and chlorite contents are somewhat higher (~5-10%). Albite (< 10%), K-feldspar (< 5%), kaolinite, and goethite are the typical minor components with amorphous material (~5-10%). Aragonite is present only in sample B18 (Be-L3).

In the clay fraction (< 2 μm) of the sediments, varying amounts of smectite, illite, chlorite, and kaolinite are present (Fig. 11). Palaeosol samples can be characterized by a smectite-dominance compared to loess samples which contain higher amounts of illite (especially Be-L1 samples). The entire section shows no obvious variation in kaolinite content. Chlorite content is generally low, and slightly decreases upwards.

The quartz-normalized bulk kaolinite content shows systematic variations with lithology, especially in the lower and middle part of the Beremend section (corresponding to OLS). The bulk kaolinite/quartz ratio increases upwards in loess

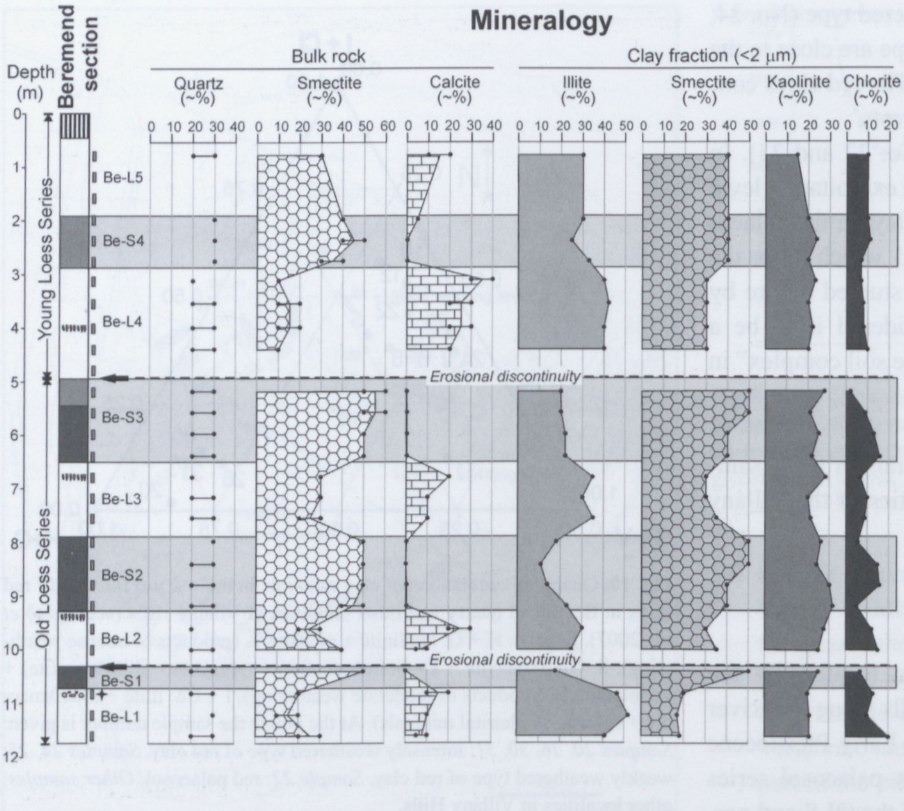


Fig. 11. Bulk-rock and clay (< 2 μm fraction) mineralogy (~%) of the loess and palaeosol samples, Beremend section, Hungary. For the legend see Fig. 5.

horizons, whereas the same ratio decreases in palaeosol layers (Fig. 12; gray arrows). As a palaeoproxy indicator, changes in bulk kaolinite/illite (kao/ill) ratio show significant differences between the Beremend palaeosol (bulk kao/ill > 1) and loess (bulk kao/ill < 1) samples suggesting fluctuations in the intensity of coeval continental hydrolysis (Fig. 12). Based on clay mineralogy, the same stratigraphic pattern in the kao/ill ratio is apparent. In the lower and middle parts of the section OLS, however, the kao/ill ratios in palaeosols are significantly higher than those of fossil soil Be-S4 (YLS). Synchronous changes in the values of smectite/illite (sme/ill), smectite/(illite + chlorite) (sme/(ill + chl)) and smectite/ kaolinite (sme/kao) ratios are also observed.

As a detrital component, kaolinite, the most common product of plagioclase decomposition during subtropical to tropical (hot and humid) climate (Weaver, 1989), is mainly considered to be derived from ferrallitic soils which are well developed in a plain environment where hydrolysis processes are very active (Liu *et al.*, 2005). On the other hand, corresponding to diagenetic origin, under warm, semi-humid to humid climatic conditions (precipitation > 400 mm/yr), extensive meteoric water flushing can result in the dissolution of detrital silicates (*e.g.*, feldspars) and formation of kaolinite (Weaver, 1989). If post-depositional weathering of detrital silicates was the major source of kaolinite in loess and palaeosol, kaolinite should be pervasively formed throughout loesses and palaeosols (Jeong *et al.*, 2008), reflecting higher kaolinite abundances in the palaeosol samples. The Beremend section, however, shows no obvious varia-

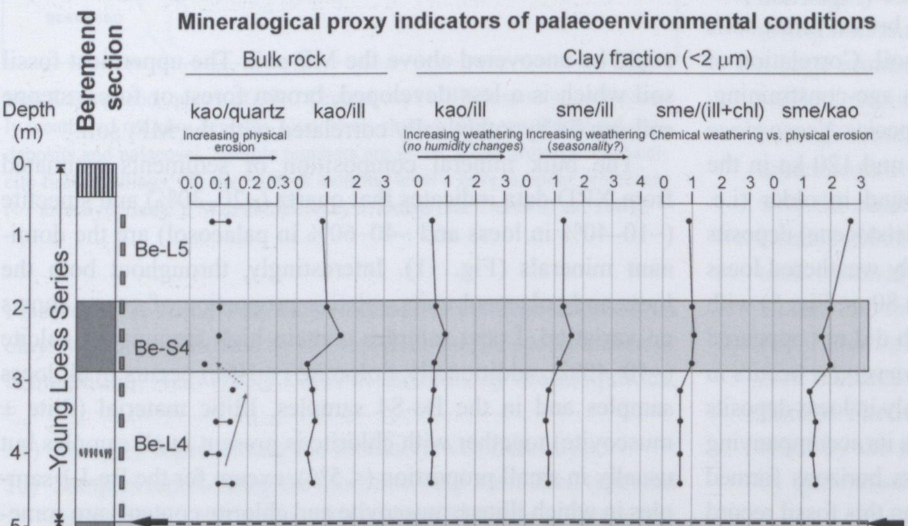


Fig. 12. Mineralogical proxy indicators of palaeoenvironmental conditions, Beremend section, Hungary. Abbreviations: kao = kaolinite; ill = illite; sme = smectite; chl = chlorite. For the legend see Fig. 5.

tion in kaolinite content with lithology (Fig. 11). Additionally, Viczián (2007) suggested that basal red clay layers of the Middle Pleistocene Paks Loess Formation at Beremend formed under warm and dry climate in a palaeoenvironment characterized by similar climatic and ecological conditions to those of tropical savannah, steppe or forest steppe. Thus, it is clear that kaolinite in the Beremend loess–palaeosol section is mostly a detrital mineral derived from active erosion of inherited clays from reworked sediments.

As far as possibility of *in situ* reworking of kaolinite is concerned, in SE Transdanubia, terrestrial kaolinitic red clays (Beremend Member of Tengelic Red Clay Formation; Fig. 5) represent a weathering crust formed on the karstified surface during a warm and humid (subtropical or monsoon) climatic period of the Late Pliocene. Persistence of huge amounts of kaolinitic palaeoweathering material in the landscapes over geological times may seriously alter the palaeoclimatic signal of kaolinite in the sedimentary record (Thiry, 2000). Therefore, kaolinite contents (relative abundance of kaolinite and kao/ill ratio) could reflect the magnitude of physical erosion occurred in the Pannonian Basin during the Pleistocene, instead of reflecting contemporary climate changes.

According to Újvári *et al.* (2008), source material of the Pleistocene loess deposits (YLS) in SE Transdanubia must have been at least partially recycled and well homogenized during fluvial and subsequent eolian transport processes. Reworked sedimentary sources were comfirmed by Buggle *et al.* (2008) as well. Weathering products of the Carpathian mountain range, drained by the Tisza River and several smaller Danube tributaries, and of the Austroalpine basement nappes, drained by the Drava River, appeared to be possible source areas (Buggle *et al.*, 2008). Accordingly, bulk kao/quartz ratio (Fig. 12) can indicate the intensity of physical erosion occurred in the source area where quartz was a common mineral present in sedimentary deposits. Both illite and chlorite may be derived from the degradation of muscovite and biotite from the erosion of sedimentary deposits (Weaver, 1989; Viczián, 2007). Consequently, illite and chlorite can be considered as mainly primary minerals and they are also representative of the physical erosion (Liu *et al.*, 2005). This result is in good agreement with the interpretation of Viczián (2002, 2007), who concluded that clay minerals (especially illite and chlorite) are essentially detrital in the Pliocene to Pleistocene pelitic sediments of the Great Hungarian Plain and SE Transdanubia.

In general, smectite can be produced by chemical alteration of parent aluminosilicates and ferromagnesian silicates under seasonally wet and dry climatic conditions, and is considered to be a product of weak to moderate weathering (Gallet *et al.*, 1998; Liu *et al.*, 2005; Viczián, 2007; Jeong *et al.*, 2008). In a Chinese loess–palaeosol section developed under monsoonal climate, Jeong *et al.* (2008) reported that illite content is higher in loess, whereas relative abundance of smectitic material is higher in intervening palaeosols. They concluded that most of the minerals in loess deposits were preserved with very weak or no chemical weathering after deposition, but intervening palaeosols were slightly weathered with carbonate dissolution, calcite reprecipitation, and phyllosilicate alteration. In some Beremend loess samples, high bulk calcite content suggests that loess is moderately altered with calcite reprecipitation, but rare presence of aragonite could suggest a relatively pristine origin of other loess samples with weak chemical weathering. Additionally, there is no evidence for post-depositional silicate weathering in loess (*e.g.*, detrital origin of illite, chlorite, and kaolinite as discussed above; relatively high albite content). In the Beremend palaeosol samples, moderate post-depositional weathering is reflected by ubiquitous carbonate dissolution (Fig. 11; bulk calcite content). Regarding clay mineralogy, relative abundance of smectite and the sme/ill ratio is significantly lower in loess samples relative to palaeosol samples (Figs. 11 and 12), suggesting slight climatic fluctuations during the evolution of the studied sequence. Smectite and mixed-layer illite/smectite with smectite-rich composition may be the product of moderate weathering of detrital phases (especially plagioclase) at both source and depositional sites under relatively dry climatic conditions (Weaver, 1989; Viczián, 2007). Therefore, sme/(ill + chl) and sme/kao ratios are adopted here as clay mineralogical indicators to reconstruct history of chemical weathering versus physical erosion (Liu *et al.*, 2005).

In the Beremend section, variations in sme/ill, sme/(ill + chl), and sme/kao ratios show similar general trends (Fig. 12). The relatively higher ratios, observed in palaeosols, suggest a strengthened chemical weathering and weak physical erosion. By contrast, lower ratios in loesses, indicate intensified physical erosion and weakened chemical weathering. Fluctuation of erosion rate is also supported by variations of bulk kao/quartz ratio. Significantly lower values of mineralogical proxy indicators in the upper part of the Beremend section may indicate a climate deterioration with decreasing rates in continental erosion and chemical weathering from the OLS to YLS in SE Transdanubia.

Day two

2.3 Field stop 3: Pécs-Vasas, open pit coal mine: Clay minerals of the Lower Liassic coal complex of Mecsek Mts.

The Coal Complex (Mecsek Coal Formation) can be subdivided vertically into lacustrine, fluvial and marine "small cycles" (tracts) of Hettangian and Lower Sinemurian age (see Fig. 13, the palaeogeographic section by Nagy, 1969). Within these "small cycles" a series of lacustrine, fluvial-dominated deltaic (marsh, riverbed, floodplain, lagoon) and marine facies units can be reconstructed. The overlying Upper Sinemurian beds are of shallow marine facies. The thickness of the complex grows from north to the south from about 100 m to nearly

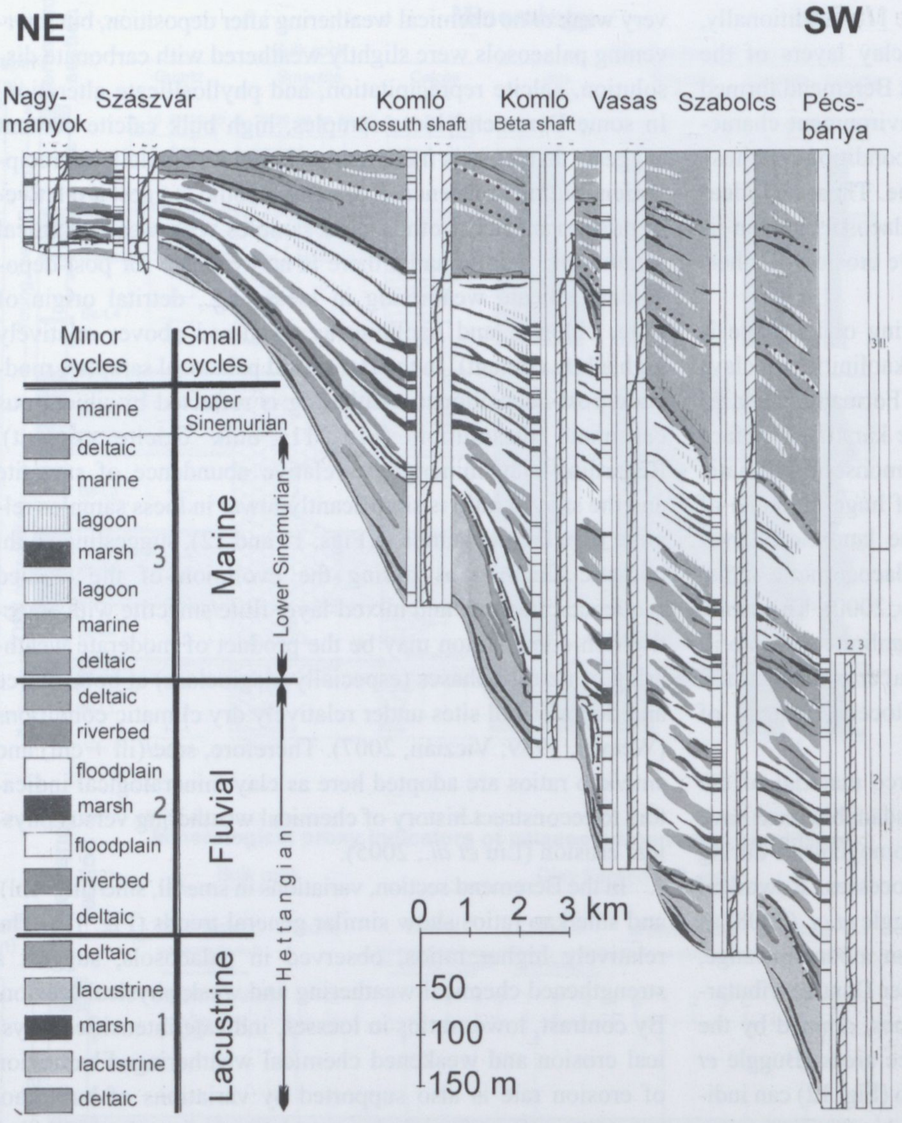


Fig. 13. Palaeogeographic NE–SW section of the Lower Liassic Coal Complex of Mecsek Mts. according to Nagy (1969). Age of the Coal Complex is Hettangian (1st and 2nd minor cycles) and Lower Sinemurian (3rd minor cycle); age of the overlying beds is Upper Sinemurian.

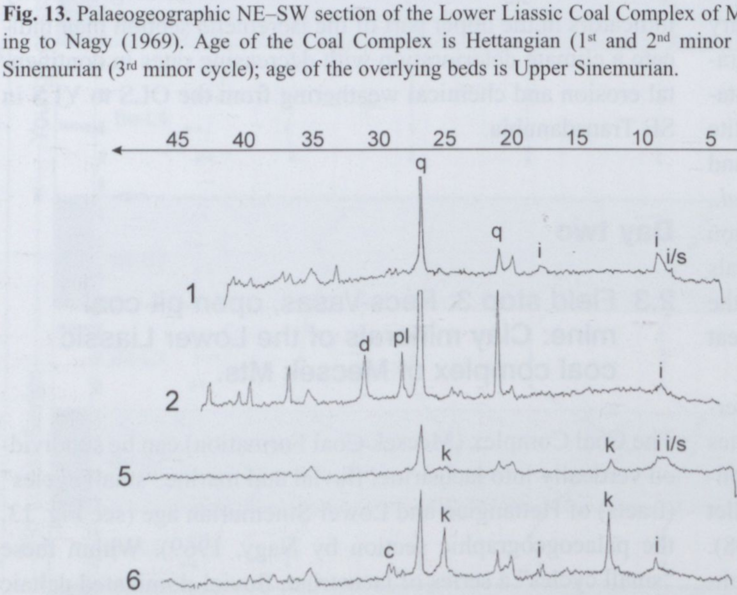


Fig. 14. Typical X-ray diffraction patterns of barren rock types according to Nagy-Melles (1966), published by Noske-Fazekas & Nagy-Melles (1969). CuK$_\alpha$ radiation. Abbreviations of minerals on the main X-ray reflections: q – quartz, i – illite, i/s – mixed-layer illite/smectite, k – kaolinite, pl – plagioclase, c – calcite, d – dolomite. See localities of the samples in the text.

1000 m. The ancient shoreline have been in the north, the main transport direction is toward the south.

The petrographic and X-ray diffraction investigations were made in the 1960's by Bárdossy, Nagy-Melles and Noske-Fazekas (see Noske-Fazekas & Nagy-Melles, 1969). The mineralogy is shown in the X-ray diagrams (Fig. 14) where the samples are arranged according to the localities from north (bottom) to the south (top). Locality and rock type of the samples:

1) Pécs, András shaft, shale,
2) Pécs, András shaft, sandstone,
5) Komló, Zobák shaft, sandstone,
6) Szászvár, sandstone.

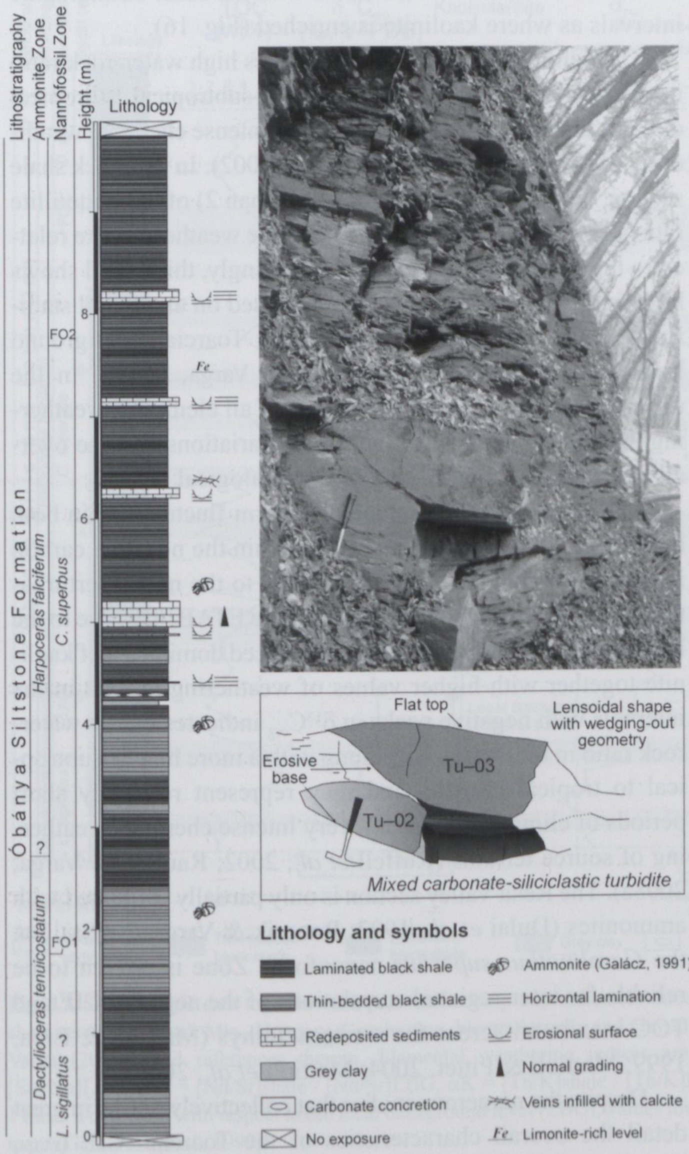
The high number of samples analysed during these studies extended to the coal and the intercalated barren rocks, outcropped by underground mine sections or key boreholes. The most important rock types were clay, marl, acid tuffaceous material and coal. Feldspar-rich (mostly potassium feldspar of granitic origin) sandstones can be observed in the north.

Typical clay minerals are kaolinite and illite with some mixed-layer illite/smectite (sample 5), somewhat independently of the rock type. Other minerals are quartz (in all samples), plagioclase, dolomite (sample 2) and some calcite (sample 6). Clay minerals are partly of detrital origin. The weathering on the source area took place under hot and humid climate. Kaolinite is more abundant near the northern margin. Chlorite occurs in the lagoon-facies rocks overlying middle and upper bed complexes, indicating marine sedimentation. Berthierine (= chamosite) is abundant in the lacustrine beds of the underlying Upper Triassic formation but less frequent in the Liassic Coal Complex.

Degree of diagenesis and coal rank are higher in the thick sequences of the southern area. The degree of crystallinity of illite and kaolinite is higher here and less in the northern areas. Mixed-layer illite/smectite of high illite proportion indicates diagenesis under deep burial (see *e.g.* sample 5).

2.4 Field stop 4: Apátvarasd, Réka Valley: Black shale and associated sediments related to the Early Toarcian Anoxic Event

In the Réka Valley, hemipelagic deposits and intercalated turbidites of the Óbánya Siltstone Formation (OSF) are exposed by a natural outcrop (Galácz, 1991; Dulai *et al.*, 1992; Némedi Varga, 1998) (Fig. 15). The hemipelagic deposits usually occur as alternating couplets of 30–350 cm thick clayey marls (mudrocks with 20–40% $CaCO_3$) and 5–40 cm thick highly bioturbated ('spotted') calcareous marls (60–80% $CaCO_3$) (Raucsik & Varga, 2008b). Beds have gradational bounding surfaces and extensive continuity. Most sandstone beds (10–70 cm in thickness) are plane-parallel, but beds with lensoidal shapes and wedging out geometries are not uncommon. Amalgamation of turbidite beds is rare. In some cases, the hybrid-arenitic bodies show graded, planar-laminated and rare cross-laminated internal structures. There is a small decrease in the amount and average thickness of turbidite beds upwards.



Essentially, clay-rich background sediments (hemipelagic clays, clayey marls and marls) dominate the section corresponding to the Early Toarcian Anoxic Event (ETAE). Here, three main petrofacies were recognized macroscopically (Varga *et al.*, 2007; Raucsik & Varga, 2008b): an organic-rich, thinly laminated (millimetre-scale) argillaceous facies (laminated black shale), a non-laminated to thickly laminated facies (thin-bedded black shale with 1–2 cm layer thickness), and occasional intercalations of fine- to coarse-grained sandstone beds (redeposited sediments) (Fig. 15). These relatively small bodies are sharp based and consist of planar-laminated and rare graded mixed carbonate-siliciclastic hybrid arenites interpreted as turbidity current deposits. Typically, these rocks have channel-like, lenticular, concave-plane geometries, with erosive bases and flat tops, reaching 1–25 cm in thickness (Varga *et al.*, 2009). This facies association attests to a low-energy basin with occasional deposition from low-concentration turbidity currents in a distal fan environment.

With respect to the bulk-rock mineralogy (Raucsik & Varga, 2008a, 2008b), the samples collected from the black shale section and from its underlying beds are predominantly composed of calcite, quartz, kaolinite, illite ± muscovite and amorphous substance. Additionally, pyrite, illite/smectite mixed-layer minerals, chlorite, rare plagioclase and K-feldspar also occur. Moreover, there are some secondary minerals such as goethite and gypsum, reflecting outcrop weathering. The samples of the black shale section have significantly higher kaolinite content relative to the underlying beds, indicating an environmental change during the ETAE.

The clay mineral assemblages of the samples collected from the underlying beds are composed of kaolinite (45–65% with an average of 53%) and illite (30–55% with an average of 39%); chlorite occurs in small quantities (from trace amounts to 25%), with traces of random (R=0) I/S mixed-layer mineral. I/S mixed-layer phase is characterized by 5% illite content in the sense of Środoń (1984). Kaolinite/illite ratios range from 0.8 to 1.9 with an average of 1.5, which can be regarded as a local background level.

The clay fraction of the samples from the black shale interval is also dominated by kaolinite. The clay mineral assem-

Fig. 15. Simplified lithological column of the Réka Valley section of the Lower Toarcian black shale, Óbánya Siltstone Formation, Mecsek Mts., Hungary. Graphic log and biostratigraphy from Raucsik & Varga (2008a) and references therein. Additional bioevents are (FO1) the first occurrence (FO) of the nannofossil *Carinolithus poulnabronei*; (FO2) the FO of the nannofossils *Watznaueria colacicchii* and *W. fossacincta* (Raucsik & Varga, 2008a). In many Tethyan areas, *Carinolithus poulnabronei* first occurs in the Lower Toarcian (tenuicostatum Zone), shortly before the FO of *C. superbus* (Mattioli & Erba, 1999). *Watznaueria colacicchii* and *W. fossacincta* were first observed shortly before the FO of *Discorhabdus striatus*, which is a good biostratigraphic marker for the exaratum/falciferum ammonite Subzone boundary (Mattioli & Erba, 1999; Mattioli & Pittet, 2004; Mattioli *et al.*, 2004). The *C. superbus* nannofossil Zone, ranging from the FO of *C. superbus* to the FO of *D. striatus*, allows precise correlation of the interval in which the maximum in TOC and the negative excursion of $\delta^{13}C$ are observed (Mattioli & Pittet, 2004). Photo and facies interpretation show the geometry of the intercalated turbidites (hammer for scale).

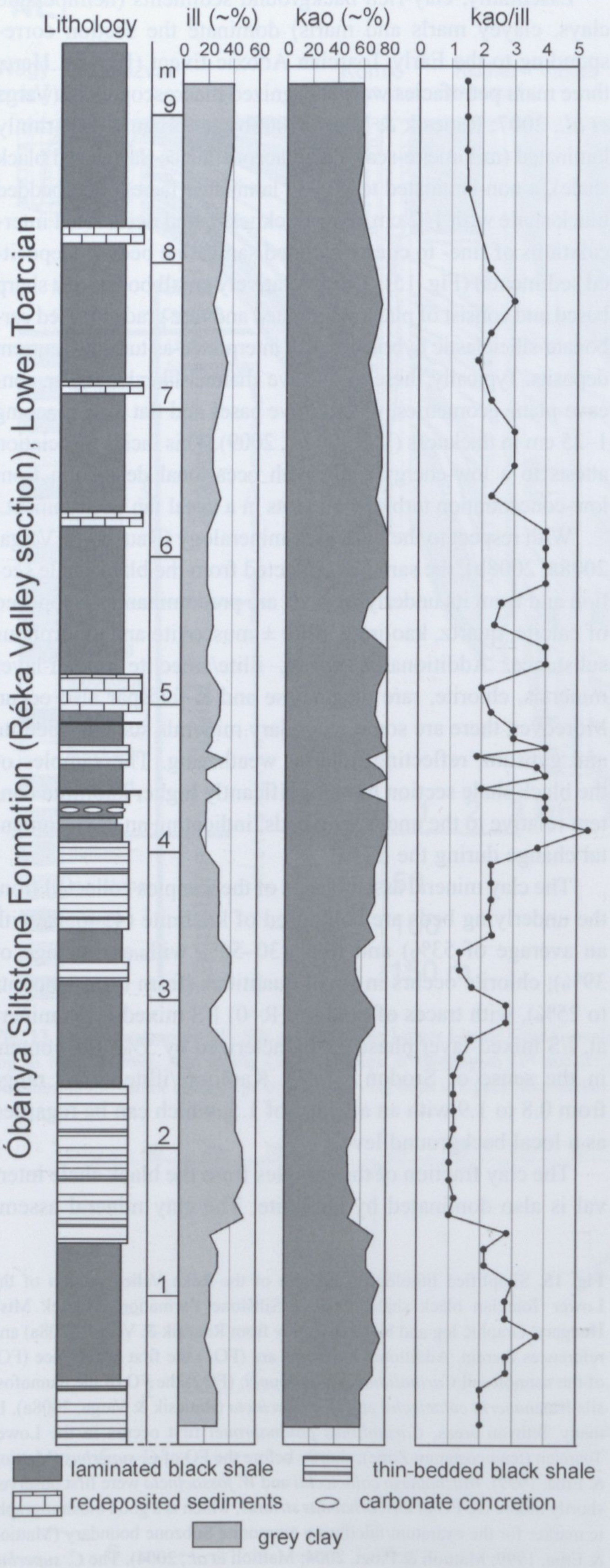


Fig. 16. Lithology (see legend) and clay mineralogy based on examination of 69 samples of the Lower Toarcian Óbánya Siltstone Formation (Réka Valley, Mecsek Mts., Hungary). Abbreviations: ill – illite; kao – kaolinite; kao/ill – kaolinite/illite ratio

blages are composed mainly of kaolinite (50–80% with an average of 67.5%) and illite (15–50% with an average of 30%); random (R=0) I/S mixed-layer mineral occurs in small quantities (from trace amounts to 5–10%), sometimes with traces of chlorite. Mixed-layer I/S is characterized by 5–10% illite content in the sense of Środoń (1984). The kaolinite/illite ratio varies strongly between 1.0 and 5.3 (Fig. 16).

Based on the high-resolution clay mineralogical composition, a stratigraphic pattern in the distribution of clay minerals is apparent (Fig. 16). In the lower part of the black shale section studied (from the base to ~3.3 m), some argillaceous intervals (laminated black shale) are relatively enriched in kaolinite, whereas some calcareous intervals (thin-bedded black shale) contain more illite. From ~3.3 to ~7.7 m, a kaolinite-rich middle part can be distinguished. Its further division shows a lower interval which is characterized by a rapid increase in the proportion of kaolinite (up to 80% of the clay fraction), and an illite-poor (less than 35%) upper interval. In the upper part of the section (from ~7.7 to the top), the proportion of illite increases, while that of kaolinite decreases upward. High values of the kaolinite/illite ratio occur in the same stratigraphic intervals as where kaolinite is enriched (Fig. 16).

The dominance of kaolinite indicates high water-rock ratio in the source area along with a humid-subtropical to tropical climate, and may represent a period of intense chemical weathering of source terrains (Ruffell *et al.*, 2002). In the black shale section, levels with high values (more than 2) of kaolinite/illite ratio suggest time intervals with extreme weathering rate related to the oceanic anoxic event. Interestingly, this signal shows high frequency fluctuations superimposed on an overall stabilization and return to the local Early Toarcian background level (kaolinite/illite=1.5; Raucsik & Varga, 2008a) in the upper part of the section. The curves of all elemental weathering indices display many small-scale variations, but the overall trend coincides with the clay-mineralogical results.

Our proxy data reveal that short-term fluctuations in both humidity and weathering intensity within the negative carbon isotope excursion (CIE) can be related to the major perturbation to the global carbon cycle during the ETAE. Relative to the local background value, the more enhanced dominance of kaolinite together with higher values of weathering indices in the intervals with negative peaks in $\delta^{13}C_{org}$ indicates higher water-rock ratio in the source area along with a more humid-subtropical to tropical climate, and may represent relatively short periods of climatically driven, very intense chemical weathering of source terrains (Ruffell *et al.*, 2002; Raucsik & Varga, 2008a). The Réka Valley section is only partially calibrated with ammonites (Dulai *et al.*, 1992; Raucsik & Varga, 2008a), but the *Carolinothus superbus* nannofossil Zone is proven to be reliable for inter-regional correlations of the negative CIE and TOC maximum across the western Tethys (Mattioli & Erba, 1999; Mattioli & Pittet, 2004; Mattioli *et al.*, 2004).

Despite the numerous studies that collectively define in great detail the overall characteristics of the Toarcian CIE (*e.g.*, Hesselbo *et al.*, 2000; Jenkyns, 2003; Mattioli & Pittet, 2004; Kemp *et al.*, 2005; Cohen *et al.*, 2007; Pearce *et al.*, 2008; Sabatino *et al.*, 2009), there is currently no consensus concerning its duration, which has been estimated as between 250 ka and 1000 ka (Suan *et al.*, 2008). Assumed a longer duration of the CIE (Mattioli & Pittet, 2004; Mattioli *et al.*, 2004; Suan *et al.*, 2008), abrupt and cyclical negative shifts in $\delta^{13}C$ took place in less than 20 ka, suggesting that orbitally-paced pulses of carbon release may have occurred at the base of the CIE (Suan *et al.*, 2008). Based on this explanation, our proxy data indicate that the short-term climate fluctuations may have lasted less than 20 ka. On the other hand, the pre-cession-based time scale (Kemp *et al.*, 2005; Cohen *et al.*, 2007), corresponding to shorter duration of the CIE, suggests that the duration of 'stage 2' was ca. 120 ka and involved several sudden shifts in $\delta^{13}C_{org}$ ca. –1‰ to ca. –3‰ that took place in as little as ca. 650 years (Pearce *et al.*, 2008). If this explanation is correct, the palaeoproxy data reported here indicate that the changes in humidity and weathering rates during the ETAE occurred very rapidly, apparently in no more than ca. 2–4 ka, supporting the previous hypothesis (Jenkyns, 2003; Pearce *et al.*, 2008).

In the upper part of the Réka Valley section, the oscillatory pattern of proxy indicators (Fig. 17) is typical of non-steady state weathering conditions, where active tectonism permits erosion of all zones within weathering profiles (Nesbitt *et al.*, 1997). In close agreement with intensified rift-related tectonic activity in the European and adjacent regions during the ETAE (Hesselbo *et al.*, 2000), non-steady-state weathering occurs where climate and tectonism vary (Nesbitt *et al.*, 1997). An alternative explanation for the oscillatory pattern of palaeoproxy signals is that alternations may be the record of rapid climate changes occurring during the changeover from one 'more humid' to 'less humid' regime before stabilizing feedback mechanisms begin to operate (Ruffell *et al.*, 2002).

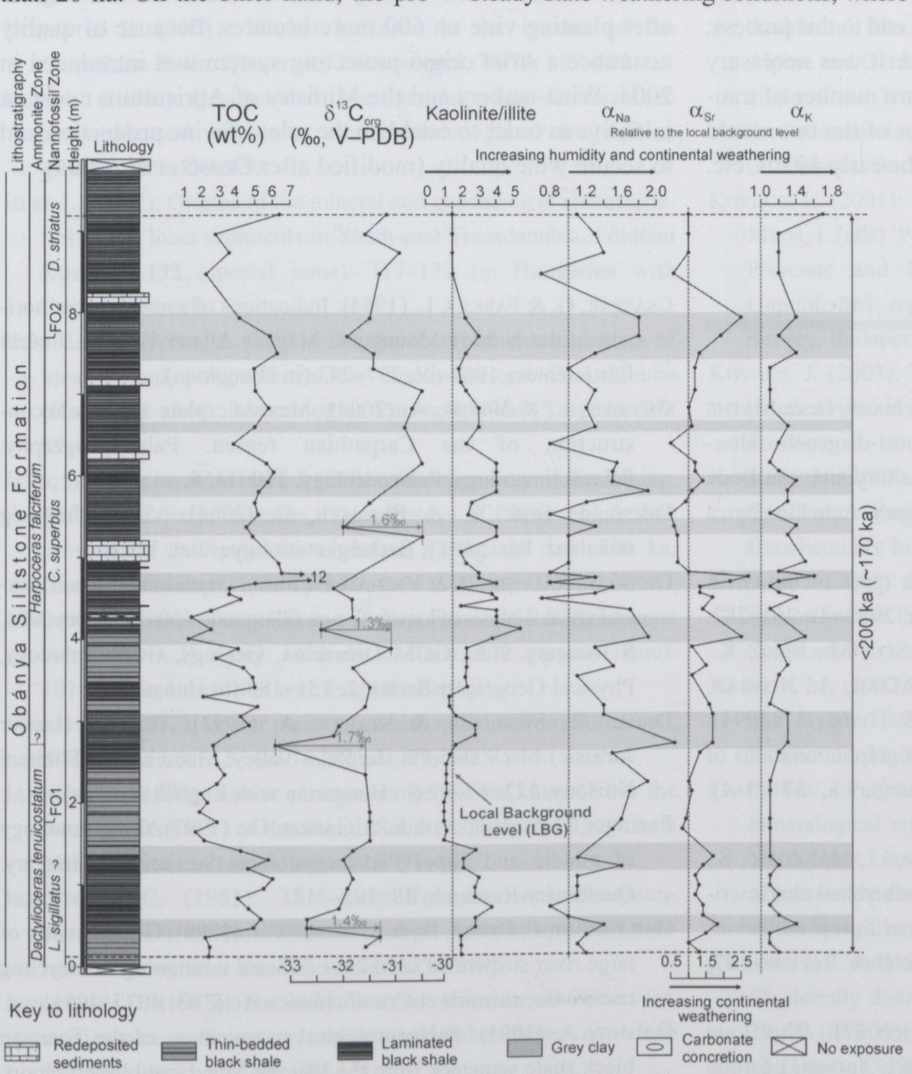


Fig. 17. Stratigraphic data together with palaeoclimatic proxy indicators through the Réka Valley black shale section, Mecsek Mts., Hungary. Graphic log, biostratigraphy and clay mineralogy from Raucsik & Varga (2008a) and references therein. Elemental weathering indices are αNa = [Sm/Na]shale / [Sm/Na]LBG, αSr = [Nd/Sr]shale / [Nd/Sr]LBG, αK = [Th/K]shale / [Th/K]LBG). Values greater than 1 mean a depletion with respect to the local background level (LBG), values lower than 1 mean an enrichment (Gaillardet *et al.*, 1999).

2.5 Cultural programmes

Day one: Bath and swimming in Harkány spa.

Besides grape- and fruit-growing agricultural lands, further natural treasures are thermal and medicinal waters that let spa culture develop. Waters of different composition and temperature in the karstic area of Villány Hills are in close subsurface connection. Meteoric water percolating through the rock warms up, its temperature rises by 1 °C in every 20–22 metres, sometimes 12.5 metres, especially in the southern foreland of the hills. The water streaming in the deep leaches large amounts of elements from the basement-forming rocks. The most important karst water in the area, the thermal water of Harkány is carried from several wells to the baths. It contains 200 mg/l dissolved material expressed in sodium equivalent. It gains the healing power from the presence of reduced sulphur with a concentration of 8–9 mg per litre (modified after Dezső *et al.*, 2004).

Day two: Dinner and wine-tasting in Villány.

Production for the market started on Roman villa farms from the 2nd century in Pannonia. These groups of buildings were centres of large estates and they were also engaged in vine growing.

In the Medieval ages wine trading played an important role in the rise and income gaining of market-settlements (oppidums) – as it is proven by farm registers also. Turkish tax records shown that despite population decrease during the 16–17th centuries, in years of peace the leading role of vine growing and wine trading survived in the area. Turkish officers in fortress of Siklós were mainly Bosnians and Albanians. Their origin from the W Balkan suggests that they could have helped the introduction of 'Kadarka' grape. After the expulsion of the Ottomans (1687) settling of German immigrants made viniculture prosper. In the middle of the 19th century the building of railway lines enabled wine from Villány to get almost all parts of the world. Vine grower farmers took advantage of this circumstance successfully. The extent of land used in vine cultivation was the biggest in the second half of the 19th century. Wines from Villány gained world fame; they proved their quality at many world championships. Huge wine cellars were built all around the Villány Hills.

In the 1880s phylloxera epidemics put an end to this process: about 60 percent of the vine was destroyed. It was necessary to breed and plant new vine varieties. Later a number of traumas hit the farmers: losing markets because of the two world wars, the large crash of world economy in the early 1930s, etc. After World War II collectivisation and the relegation of German-speaking "Swabian" inhabitants almost totally disorganised the former farming structure based on experience of centuries.

As soon as it was possible, in the 1960s, farmers cultivated their own former estates again, although bottling and trading were reserved for state-controlled companies. Emphasis was put on mass production mainly to satisfy the export to countries of the "Eastern block", *i.e.* to the countries more or less controlled by the Soviet military, political and economic power. This mass production system was typical until the early 1990s, then, after the changes in politics, a spectacular development started in the Villány wine district despite the lack of infrastructure, because of the production of quality wines based on family traditions also survived during the disadvantageous decades.

The election of the vine-growing community ('hill community') as the form of administration has been compulsory since 1995. There are six communities with a total area of 1600 hectares in the Villány district, and their extent grew after planting vine on 600 more hectares. Because of quality assurance a strict origin-protecting system was introduced in 2004. Wine-makers and the Ministry of Agriculture made an initiative in order to establish the rules of wine production and to secure wine quality (modified after Dezső *et al.*, 2004).

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Appendix – Itinerary for MECC2010 Field trip

Friday, August 27, 2010 (Day 0)

17.30–20.00	Travel from Budapest to Pécs
Dinner and accommodation in Pécs	

Saturday, August 28, 2010 (Day 1)

09.00–11.00	Field stop 1: Kővágószőlős, visit to the Mecsekérc Ltd. and Geochem Ltd.
11.00–12.00	Travel to Beremend
12.00–13.00	Lunch break in Beremend
13.00–14.00	Field stop 2: Beremend: Pliocene red clay and Pleistocene loess/palaeosol series
14.00–15.00	Travel to Harkány
15.00–18.00	Bathing and swimming in Harkány spa
18.00–19.00	Travel to Pécs and dinner
	Accommodation in Pécs

Sunday, August 29, 2010 (Day 2)

10.00–11.00	Pécs, visit to the Zsolnay Museum
11.00–13.00	Field stop 3: Pécs-Vasas: Lower Jurassic coal-bearing sediments
13.00–14.00	Lunch break in Pécsvárad
14.00–16.00	Field stop 4: Réka Valley: Lower Toarcian black shale
16.00–17.00	Travel to Villány
17.00–19.00	Wine tasting in Villány
19.00–21.30	Travel to Budapest